

193 nm Photodissociation of Propylene Sulfide Using Synchrotron Radiation

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INTRODUCTION

Propylene sulfide (*c*-C₃H₆S), a three-membered heterocyclic compound, is a derivative of ethylene sulfide. The thermal decomposition of *c*-C₃H₆S was investigated in a flow system at various temperatures.¹ Formation of S and C₃H₆ was detected at 600 °C. At higher temperatures, conversion of propylene sulfur into *cis*- and *trans*-prop-1-ene-1-thiol was observed. A mechanism involving initial C-S bond breaking, followed by 1,2-hydrogen shift, was suggested by authors. A similar three-membered compound, ethylene sulfide, was studied at 193 nm photodissociation by using photofragmental translational spectroscopy (PTS) probed via synchrotron radiation. Some interesting channels, i.e., S(¹D) + C₂H₄(¹A_g) and S(³P) + C₂H₄(³B_{1u}), were discovered.²

Here we have measured the time-of-flight spectroscopy and some photoionization efficiency spectra (PIE) of photofragments from photolysis of *c*-C₃H₆S, using photofragmental translational spectroscopy and undulator synchrotron radiation of the Chemical Dynamics Beamline at the Advanced Light Source.

EXPERIMENTAL

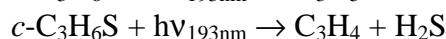
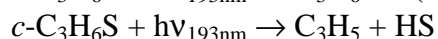
The experiment was completed at beamline 9.0.2.1 of the Advanced Light Source using a rotatable source molecular beam apparatus described in detail elsewhere.³ A pulse molecular beam of 10% propylene sulfide seeded in helium was skimmed twice and intersected at 90° with the 193 nm photolysis laser. Photofragments formed by 193 nm photodissociation entered the detector chamber region (1×10⁻¹⁰ Torr), and were photoionized using the tunable synchrotron radiation. The tunability of the light source allows for selective ionization of products and very low background counts, and also allows for measuring the PIE spectra of photoproducts. The photoionized products were mass selected by using a quadrupole mass filter and the ions were counted with a Daly ion counter. An multichannel scaler (MCS) was used to measure the time-of-flight (TOF). Propylene sulfide (98%) was obtained from Fluka and used without further purification.

RESULTS AND DISCUSSION

The TOF spectra at *m/e* 59, 42, 41, 40, 34, 33, 32, and 15 from 193 nm photodissociation of *c*-C₃H₆S were measured at different angles (15 - 40°). They correspond to C₂H₃S, C₃H₆, C₃H₅, C₃H₄, H₂S, HS, S, and CH₃ respectively. In all the TOF spectra presented here, the open circles represent the experimental data, the color lines are single channel contributions to the forward convolution fit, and the black lines are the overall fit to the data. A forward convolution fit to data was used to get center of mass translational energy distributions, P(E).⁴

Five primary dissociative channels have been discovered, as summarized by processes 1-5.





$$\Delta H_{\text{avai}} = 54 \text{ kcal/mol} \quad (3)$$

$$\Delta H_{\text{avai}} = 76 \text{ kcal/mol} \quad (4)$$

$$\Delta H_{\text{avai}} = 110 \text{ kcal/mol} \quad (5)$$

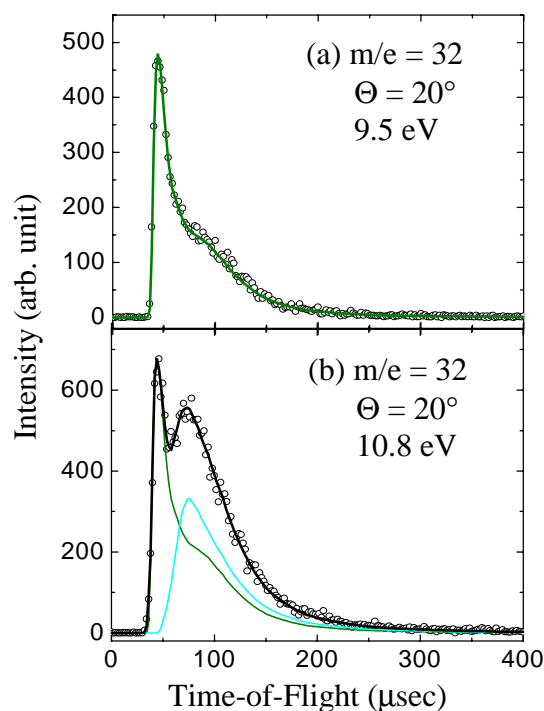


Fig. 1 TOF spectra of $m/e = 32$ at the scattering angle of 20° and (a) 9.5 eV probe energy, and (b) 10.8 eV probe energy.

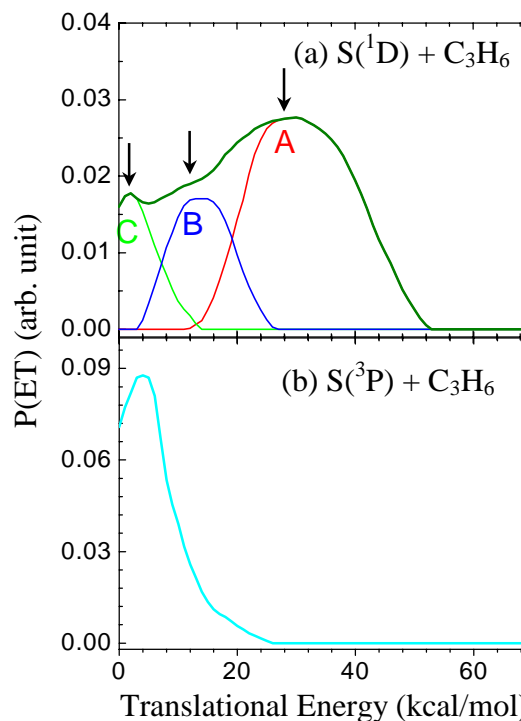


Fig. 2 The translational energy distribution for (a) the $\text{S}({}^1\text{D}) + \text{C}_3\text{H}_6$ channel, and (b) $\text{S}({}^3\text{P}) + \text{C}_3\text{H}_6$ channel.

Fig. 1 shows TOF spectra of $m/e = 32$ at the scattering angle of 20° and the indicated photon energy. A translational energy distribution shown in Fig. 2(a) was used to fit TOF data in Fig. 1(a). This corresponds to a channel of $\text{S}({}^1\text{D}) + \text{C}_3\text{H}_6$. Because the probe energy used here is below the ionization potential of $\text{S}({}^3\text{P})$. Three components were observed in Fig. 1(a). It is very similar to that of ethylene sulfide.² Furthermore, the experiment was repeated at 10.8 eV probe energy, the TOF spectra is shown in Fig. 1(b). An additional translational energy distribution was used to fit the data. It is shown in Fig. 2(b), which corresponds to the $\text{S}({}^3\text{P}) + \text{C}_3\text{H}_6$ channel. The dissociation mechanism is also similar to that of ethylene sulfide.

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This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division of the US Department of Energy under contract No. DE-AC03-76SF00098. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division of the US Department of Energy under the same contract.

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